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15 pages

NASA TECHNICAL MEMORANDUM

NASA TM-88470

11-18371

ELECTRODES WITH FIBER STRUCTURE

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Translation of "Elektroden mit Faserstruktur," Elektrotechnische Zeitschrift, Vol. 104, No. 21, 1983, pp. 1098-1101.

(NASA-TM-88470) ELECTRODES WITH FIBER
STRUCTURE (National Aeronautics and Space
Administration) 15 p CSCI 09C

N86-29136

G3/93 43465
Unclas

STANDARD TITLE PAGE

1. Report No. NASA TM-88470	2. Government Accession No.	3. Recipient's Catalog No.
4. Subject Terms ELECTRODES WITH FIBER STRUCTURE	5. Reissue Date July, 1986	6. Performing Organisation Code
7. Author(s) Benczur-Ürmösy, G. Berger, F. Haschka, Deutsche Automobil- gesellschaft mbH	8. Performing Organisation Report No.	10. Work Unit No.
9. Performing Organisation Name and Address Leo Kanner Associates, Redwood City, California, 94063	11. Contract or Grant No. NASW-4005	12. Type of Report and Period Covered Translation
12. National Aeronautics and Space Admin- istration, Washington, D.C. 20546	14. Sponsoring Agency Code	
13. Supplementary Notes Translation of "Elektroden mit Faserstruktur," Elektrotech- nische Zeitschrift, Vol. 21, No. 104, 1983, pp. 1098-1101.		
16. Abstract An electrode framework with a fiber structure, universally applicable in alkaline storage battery systems, was developed and readied for production. Storage batteries with these electrodes present higher energy and power densities and are economical to produce. The design is applicable to all rechargeable storage batteries and might replace the previous variety of designs.		
17. Key Words (Selected by Author(s))	18. Distribution Statement Unclassified-unlimited	
19. Security Classif. (of this report) Unclassified	20. Security Classif. (of this page) Unclassified	21. No. of Pages 13
		22.

ELECTRODES WITH FIBER STRUCTURE

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/1098*

For over ten years, broad-based work has been under way on developing secondary batteries for use in electrotraction. Such research and development activities, however, concentrate not only on new systems but on existing alkaline storage batteries. They revealed a number of promising potential developments for these systems, especially in electrode design. Particularly, an electrode framework with fiber structure universally usable in alkaline systems was developed and readied for production. Accumulators with these electrodes present higher energy and power densities, and are economical to produce. The design is applicable in all rechargeable storage batteries and could possibly replace the previous variety of designs.

Significance of Electrodes

The electrodes, as the actual power source, are in the focus of battery development. In addition to the composition of the active masses, the electrode structure has particular significance, for it must fulfill a number of tasks which with optimum solutions make maximum demands on material, construction and durability. This is only incompletely possible with currently common electrodes.

Considerations on improving this situation led to an electrode structure which also takes account of recent scientific discoveries in the field.

*Numbers in the margin indicate pagination in the foreign text.

State of the Art

Pocket plates, as the oldest and still most common electrode form for alkaline batteries, enclose the active mass between strips of punched plating. Graphite must be added as a conductor to the poorly conductive active masses. The graphite oxidizes relatively rapidly in the positive nickel oxide electrode to form carbonate, consequently reducing the conductivity of the electrolyte and the loadability and lifespan of the electrodes. A low free pore volume of the active masses and the impeded current access due to the small open area of less than 25%, result generally in lower loadability, which sharply decreases further as electrode thickness increases. Because of their construction, the plates are quite heavy and unsuitable for use in traction batteries (e.g. electric streetcars). The cycle stability is especially limited in thick electrodes because of swelling.

Tube electrodes have a similar construction. The main lead in the form of a punched plate is likewise applied on the outside. It is coiled into a spiral tube ca. 6 mm in diameter, and the mass and nickel tinsel are punched in in layers from above. Finished tube electrodes do not swell as a rule, but are very expensive to manufacture and are only available as thick electrodes.

Sintered electrodes are the only ones to present a three-dimensional conductor framework of sintered nickel powder. The hollow spaces are filled with active mass in an expensive process. Special kinds of powder allow framework porosities of ca. 80% and relatively high energy density. The electrodes have high loadability and cycle stability, and are free of harmful graphite. As thickness increases, however, cycle lifespan decreases sharply, so that only the ca. 1 mm-thick sintered electrodes can be used in cells. Experiments have been undertaken to achieve a high lifespan for thicker electrodes as well

[1]. But no usable solutions are known yet.

The current state of the art knows no electrode structure that simultaneously satisfies the requirements of high loadability, cycle lifespan and energy density for a wide range of electrode thickness with a uniform technology.

Ideas on an Improved Electrode Structure

In storage electrodes, the essential processes occur at the contact surface between active mass and electrolyte. Here the electrochemical reaction occurs in which chemical energy is "reversibly" converted to electrical energy. As a rule, active masses are expensive and require correspondingly good utilization. Their non-conductive character in the discharged state poses problems. For low-loss conduction of the electrons, it is therefore desirable to surround the smallest possible areas of active mass with a metal conductor, e.g. nickel, in the form of a three-dimensional network. At the same time this gives the electrode the necessary mechanical strength. Losses during conversion to electrical energy develop mainly in transporting the current to the poles and in the electrolyte. The electrical conductivity of metals exceeds that of electrolytes by several powers of ten. To minimize losses, for the electrodes one selects small conductor cross-sections and longer paths to the poles, while on the other hand large cross-sections and short paths for the ions must be observed. The electrolyte resistance inside the electrode can be reduced by high porosity and suitable pore structure.

To improve access of the ion current to the inside of the electrode, the metal conductive framework should provide as little shielding as possible. A negative example in this sense is the punched plates used in pocket plates, which cover at least three-fourths of the geometric surface. High porosity also

facilitates electrolyte access to the inside of the electrode and increases utilization of the active mass by promoting compensation of differences in concentration developing because of electrochemical reactions inside and outside the electrode. /1099 An "ideal" electrode structure accordingly exists when a maximum active mass/conductor material contact area is combined with maximum possible porosity.

Additional requirements for electrode construction are posed by the considerable changes in volume of the active masses during charging and discharging. These act in combination as pressure on the metallic conductor framework, which causes swelling or destruction of the electrode, especially in thick electrodes [2, 3].

To satisfy these extra requirements for thick electrodes as well, a network of fibers seemed the most suitable. Compared to a rigid sintered body, such a fiber structure framework offers the advantage of the fibers' improved mobility and elasticity. As in a composite material, the active mass is embedded in the hollows of the network, whose fibers are in electrical contact with each other. They are not sintered, and can therefore better handle the volume movements of the active masses.

Thick electrodes are preferably used in storage batteries, since as the number of electrodes increases, production costs for a cell increase considerably. The development of such high-loadability and cyclically stable electrodes was also promoted by electrotraction. The light and economical batteries sought there can be achieved most readily with these electrodes.

The aforementioned ideas on the metallicly conductive fiber structure framework were first realized in positive nickel oxide electrodes. The active mass is a non-conductor in the discharged state, but a semiconductor in the charged state, with

sharp changes in volume depending on the state of discharge; the entire crystallite expands and shrinks periodically.

Nickel Oxide Electrodes on a Nickel-Fluff Basis

In the first phase of development a dendritic nickel, so-called nickel-fluff, was available. Figure 1 shows electron micrographs of nickel fluff and nickel powder, as used for sintered electrodes. The fibrous nickel allowed production of fiber frameworks with ca. 90% porosity, 2 to 3 mm thick. For production, the fluff grains were poured into a pressing mold, slightly compressed and sintered. By an electrochemical method, the active mass was precipitated in the pores. Such electrodes, ca. 2 mm thick, proved to have loadability practically as good as the considerably thinner sintered film electrodes. The influence of electrode thickness was reduced decisively by the fiber framework.

Also significant was the relatively low proportion of conductive framework in the total weight of the electrodes. The capacity per unit weight of the fluff electrodes exceeded that of sintered films and made them attractive for electrotraction (Table 1).

Lifespan was tested in cyclical operation with complete discharges. During the 2000 cycles tested there was no noteworthy loss in storage capacity or loadability. The electrodes presented no swelling and did not change externally. The results essentially confirm the correctness of the fiber design.

For practical testing, nickel oxide fluff electrodes were used in a nickel/zinc (Ni/Zn) traction battery with an energy content of 15 kWh. With it, a VW Golf first drove distances of over 120 km under realistic running conditions. The specific energy content was 45 Wh/kg for the two-hour discharge [4]. /1100

Table 1. Capacity per unit weight and area of nickel oxide electrodes (2-hour discharge).

Elektrode a	Dicke c mm	flächenbezo- gene Kapazität d Ah/cm ²	gewichtsbezogene Kapazität e gef. trocken g	
			f elektrolyt- gefüllt Ah/kg	g Ah/kg
Sinterfolie b	1	0,028	74	88
Fluff	2	0,063	110	140
Fluff	3	0,086	100	130

Key: a. electrode b. sintered film c. thickness
d. capacity per unit area e. capacity per unit weight
f. electrolyte-filled g. dry

Fiber Structure Electrodes on a Carbon-Fiber Basis

In fluff electrodes, the necessary sintering was a process engineering drawback. To this was added limited availability of fluff material. Carbon fiber frameworks offered a favorable expansion of the fiber structure concept in the direction of larger electrode thicknesses. They allowed the influence of fiber thickness and density, and of the arrangement of the three-dimensional structure, to be studied and optimized.

Coating the fiber framework with nickel required a special galvanic process to precipitate nickel even inside thick frameworks. Conductivity and weight of the framework could be adapted to the respective application (electrotraction, starter batteries). The finished frameworks had a high mechanical strength despite a high porosity of up to 95%. The remaining volume was filled by fibers with a length between 200 and 800 m/cm³, enclosing correspondingly small hollows provided for the active mass. Figure 2 gives an impression of the close-meshed nickel fiber framework. The mass was deposited in the framework by electrochemical precipitation. Other conventional methods can be used just as well.

a)



Fig. 1. Scanning electron micrograph of nickel fluff (a) and nickel powder (b) (magnification 1:1000)

b)

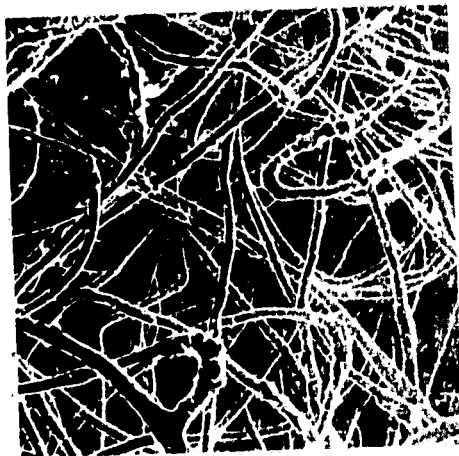


Fig. 2. Nickel fiber structure framework (magnification 1:100)

Table 2. Capacity values of nickel oxide electrodes (2-hour discharge) 1 = electrode filled with electrolyte.

Elektrode a	Dicke e mm	flächenbezogene Kapazität f Ah/cm ²	gewichtsbezo- gene Kapazität g Ah/kg ¹)
Faser b	1,0	0,027	95
Faser b	2,5	0,065	118
Faser b	4,5	0,110	117
Sinter c	1,0	0,028	74
Taschen d	2,5	0,030	45
Taschen d	4,5	0,067	65

Key: a. electrode b. fiber c. sintered
d. pocket e. thickness
f. capacity per unit area g. capacity per unit weight

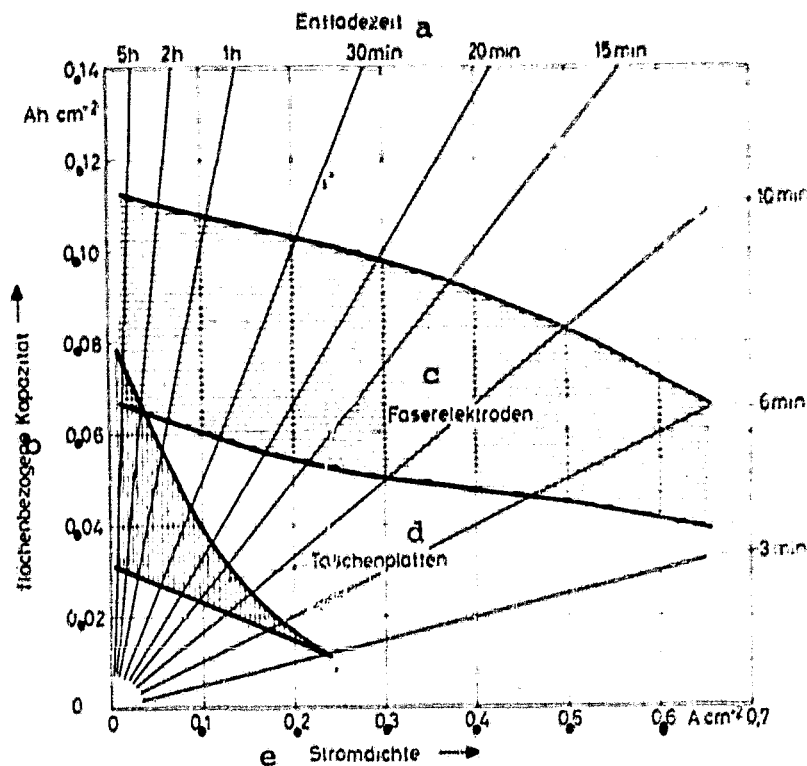
Table 3. Properties of nickel oxide electrodes with various technologies. 1 = other properties being the same

Elektrodentyp a Eigenschaft b	Röhrchen i	Taschen j	Sinter k	Faserstruktur l
Kapazität, gewichts- bezogen c	niedrig m	niedrig m	mittel n	hoch o
Ausnutzung der Masse unter Bela- stung d	niedrig m	mittel n	gut p	gut p
Dickenvariation ¹) e	nein r	begrenzt s	begrenzt s	ja t
Graphitzusatz f	nein r	ja t	nein r	nein r
Zyklusfestigkeit g	hoch o	mittel n	hoch o	hoch o
Herstellungskosten h	hoch o	mittel n	hoch o	mittel n

Key: a. electrode type b. property
c. capacity per unit weight
d. utilization of mass under load
e. variation in thickness f. graphite added
g. cycle stability h. production costs
i. tubes j. pockets k. sintered
l. fiber structure m. low n. medium
o. high p. good r. no
s. limited t. yes

ORIGINAL QUALITY
OF POOR QUALITY

Fig. 3. Loading performance of nickel oxide fiber structure and pocket plate electrodes (electrode thickness 2.5 to 4.5 mm).



Key: a. discharge time
c. fiber electrodes
e. current density

b. capacity per unit area
d. pocket plates

Loadability tests also confirmed good capacity performance for thick electrodes. Figure 3 shows a comparison of loadability performance for 2.5 mm and 4.5 mm fiber and pocket-plate electrodes. Note that the new fiber structure electrodes supply twice the capacity at the same thickness. At the same discharge rate, they carry a correspondingly larger current, yet by percentage lose less capacity than the pocket plates.

Table 2 summarizes the achieved specific data of fiber structure electrodes and the nickel oxide electrodes previously

used in alkaline cells.

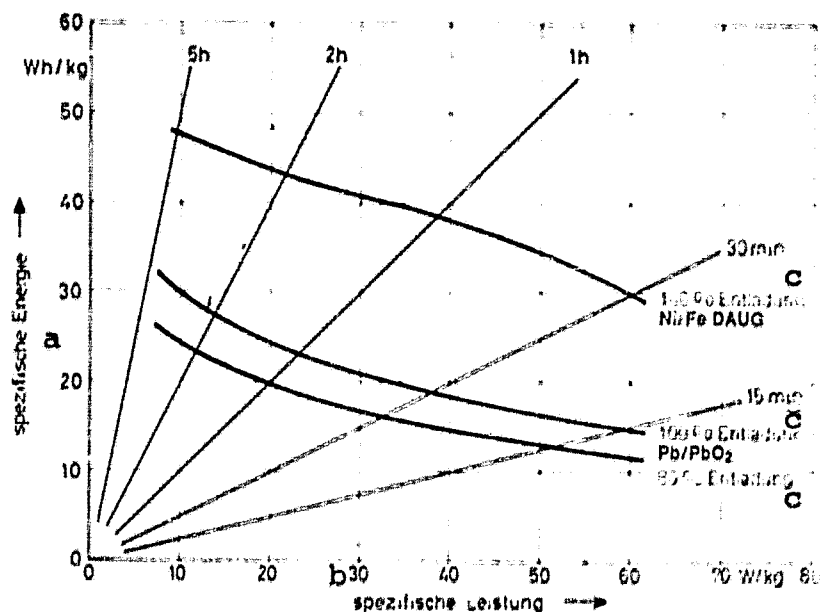
The developed fiber structure electrodes exceed previous electrodes in capacity per unit weight and area. Storage batteries with such electrodes are not only lighter, but also form the basis for more economical production. The absence of harmful graphite in the active mass is the prerequisite for acceptable durability. The electrodes were again tested with 100% depth of discharge for more than 2000 cycles, without showing swelling or other changes. This applies for electrodes 1 mm as well as 4.5 mm thick. As already noted, the high elasticity of the fiber structure framework may make this good cycle stability possible. /1101

Table 3 gives a summary evaluation of essential properties of conventional and new electrodes.

The suitability of the new electrodes in practical operation was verified in several alkaline systems. Nickel/zinc laboratory cells with these electrodes were tested for 2000 cycles without noteworthy losses in capacity, with a one-hour discharge current and 100% depth of discharge [5]. This cycle lifespan is extremely high for the system, and previously unheard of from any other development institution. Nickel/hydrogen cells presented similarly reliable performance. In this system particularly, lifespan depends almost exclusively on the quality of the nickel oxide electrode [6].

Finally, fiber structure electrodes also proved themselves in traction batteries with the nickel/iron system. These cells, with a nominal capacity of 200 Ah, contain conventional iron sintered electrodes as the negative pole. Such a battery, with a content of ca. 25 kWh (two-hour) has driven an electric auto (Mercedes T) for almost two years [7].

Fig. 4. Energy-output graph of a nickel/iron and a lead traction battery.



Key: a. specific energy
c. ___% discharge

b. specific output

The loadability performance of these batteries is shown in Fig. 4 together with the data of some lead traction batteries. The optimum-weight nickel oxide electrodes helped the system, previously known more for low energy densities, to reach 45 Wh/kg for a two-hour discharge. Thus the vehicle runs about twice as far as with a lead battery of equal weight.

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